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OKLAHOMA UNIV. NORMAN DEPT OF CHEMISTRY
SYSTEMS FOR THE STORAGE OF MOLECULAR OXYGEN - A STUDY.(U)
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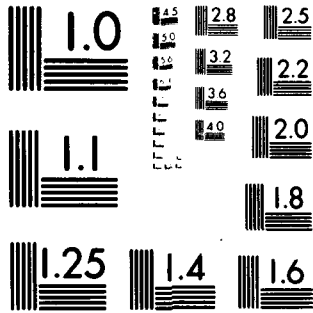
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FINAL TECHNICAL REPORT

Systems for the Storage of Molecular Oxygen

- A Study

by

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November 25, 1980

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ABSTRACT

→ A search of the current chemical literature has been performed in an effort to identify systems to generate and store molecular oxygen. Most of the current oxygen production capacity is based on the cryogenic fractionation of air; alternatives for smaller scale or more mobile situations were sought. Systems were classified according to one of four types: adsorption/adsorption, chemical reaction, formation from cheap substrate, and continuous separation. At present, only zeolite-based adsorption systems are commercially competitive; three other candidate systems for further development are identified. ↗

INTRODUCTION

Oxygen is nearly ubiquitous. The most abundant element on earth, it makes up 46.6% of the earth's crust, mostly as the oxides of various metals or semimetals. It is also one of the few elements present in nature in uncombined form. As dioxygen (O_2) it makes up 20.95 volume percent of the atmosphere (1a). Although many of the processes which require molecular oxygen can use it as it occurs in air, mixed with nitrogen and other gases, at times oxygen of higher purity is required. The uses of oxygen as an oxidizing agent range from steelmaking, oxyacetylene welding, and other industrial uses to an oxidizer for rocket propulsion systems. For many of these applications it is useful to have oxygen of 95 to 99 percent purity, rather than its normal concentration in air. Perhaps the most important role of oxygen is the part it plays in animal metabolism, serving as the oxidizer that supports the controlled combustion we know as life. Stored forms of oxygen are useful to help sustain life (primarily human) in environments and under conditions where O_2 is normally rare or unavailable. Prime examples of these situations would be activities conducted underwater or in the upper atmosphere.

The scope of this study is to investigate new methods for the separation or generation of molecular oxygen in a form that is storable. The major focus of this report will be on such systems that are cyclic or regenerable in nature, since these allow increased efficiency of operation. Small amounts of oxygen can be generated by the thermal decomposition of oxide salts such as $KClO_3$ (1b) but this type of system will not be considered here, due to the complexity of regenerating the storage medium.

Separation and storage methods can be separated into four somewhat arbitrary classes, each of which will be examined in turn. The simplest class consists of those systems which store oxygen in molecular form. These can be broken down into two types, one of which depends on physical attractions to separate and/or retain the desired product, i.e. adsorption processes. Separated from the adsorption processes by a fine line are those which rely on chemical reaction of dioxygen with the working material, but still maintain the integrity of the oxygen-oxygen bond. These can be called absorption processes to distinguish them from the purely physical processes in the first subclass. Absorption processes where the molecular oxygen unit is disrupted form the basis for the second general class. These systems store the oxygen in chemically combined form and require the reconstitution of the oxygen molecule at some stage in the process. The chemically combined form is usually very simple, e.g., a metal oxide. The third general class encompasses systems which can generate molecular oxygen from some cheap, easily reformed substrate. While the substrate (e.g., H_2O) is often not formed expressly to store oxygen, the system is defacto a cyclic storage scheme if the end use helps to replenish the substrate. Last to be considered are systems which can separate oxygen from air on a continuous basis, but have some storage capacity by virtue of their design.

Most conventional methods to produce oxygen are based on the cryogenic (low temperature) fractionation of air (2). Using these methods for over 70 years, the industry has matured with many improvements and refinements developed and put into practice throughout that time. Production in 1979 was 15.8 million metric tons in all forms, worth more than \$440 million (3).

Plants have been designed to produce both gaseous and liquid oxygen with capacities ranging from 20 to 2000 ton/day (4a). The oxygen produced is generally consumed on-site, distributed as the gas compressed to 150-200 atmospheres, or as the liquid. Some commercial oxygen production by pressure swing adsorption units (see below) is beginning to emerge, especially in remote locations and for small volume users (3,4b) where the economics are more competitive, but the total volume produced by these methods remains small.

While cryogenic methods of oxygen manufacture are currently the most economical for large-scale production and storage, there are many situations in which the necessity for large-scale operation becomes a liability. Already noted above are increases in the production of oxygen by pressure swing adsorption for applications requiring relatively small volumes of lower purity (95%) oxygen, e.g., aerobic waste treatment (4b). Other applications can be identified where portability and/or light weight would be a definite asset. Perhaps foremost among these systems generating life-support oxygen in aircraft, spacecraft or other highly mobile enclosed environments. In such systems low weight, minimum power requirements and simple logistics and/or maintenance are definite plusses.

In many combat aircraft today, for example, crew oxygen requirements are met by the controlled warming of liquid oxygen, satisfying all but the last criterion. As will be demonstrated later, some of the "new" systems under consideration have reasonable power and weight parameters while obviating the need for complex ground support procedures and equipment necessary to use liquid oxygen.

Other potential applications each have their own particular set of parameters of weight, power use, maintenance, etc., which may be optimized

by different systems in each case. Consequently, it is difficult to compare systems directly, since they are likely to be useful in different circumstances. It is more feasible to identify the best system in a particular class and note its most likely applications.

EVALUATION

Type IA: Let us first consider what is probably the simplest way of storing a molecular species--physical adsorption. All systems based on this principle have certain common features. The primary requirement is an adsorbing material and a container in which to put it. There are usually more than one of these "adsorber beds" since most processes are cyclic in nature and usually involve adsorb, desorb and regenerate steps. Other common components are the expected pumps, piping, and switching networks, as well as heating and/or cooling for the bed as necessary. Normally in adsorption processing the key step is the desorption portion of the cycle. Following is a brief summary of the four basic methods of desorbing a loaded adsorbent bed (4b). (In practice, two or more of these methods are often combined to improve performance.)

Thermal swing cycles employ a desorption temperature which is higher than the adsorption temperature (see Figure 1). Bed heating and cooling can be accomplished by circulating an appropriate temperature liquid through enclosed coils or by purging the bed with a hot or cool inert fluid.

Pressure swing cycles operate at nearly constant temperature, chosen so that desorption readily occurs when the pressure is reduced by a moderate amount. If increased capacities are desired, the desorption step can be done under vacuum. Pressure swing systems can cycle more quickly than equivalent thermal swing systems since no additional time is required for heating and cooling the adsorbent beds. The shorter cycle time thus can allow smaller bed dimensions and reduced amounts of adsorbent.

Purge gas stripping cycles involve purging the adsorbent bed with a nonadsorbable gas to reduce the partial pressure of the adsorbed gas in the space around the adsorbent, causing desorption in an attempt to reestablish the equilibrium. The mechanism is therefore similar to desorption by reducing the total

pressure (pressure swing), but is generally more efficient at higher temperatures and/or lower pressures.

Displacement cycles involve purging the bed with a fluid which is itself adsorbed, therefore displacing all or part of the previously adsorbed material. The amount of desorption is dependent on the relative adsorptivities of the displacing fluid and adsorbate. When the displacing agent is more strongly adsorbed, it will simply displace the less strongly held material which was on the adsorber. When a less strongly adsorbed fluid is used as a displacer, desorption is due both to displacement and partial pressure stripping.

The most common adsorbents used are members of a group of crystalline aluminosilicates called zeolites. Certain synthetic zeolites having carefully defined stoichiometry are honeycombed with relatively large cavities connected with adjacent ones through apertures or pores. For example, Type 4A molecular sieve contains roughly spherical cavities about 11 \AA in diameter and about 925 \AA^3 in volume, accounting for nearly half the total crystal volume. This volume is available for adsorption. The free aperture diameter in Type 4A is 3.5 \AA , allowing passage of molecules with an effective diameter as large as 4.0 \AA at normal operating temperatures (4b). Although these synthetic materials allow the design and synthesis of adsorbents with carefully controlled properties (5), it has recently become apparent that natural materials can be used in certain cases (6,7). For example, the properties of a Japanese mordenite have been extensively investigated (8). Other materials such as silica gel and activated carbon (6,9) or natural coals (10) have also seen some use.

In principle, there are two ways that adsorbent beds could be used to produce an oxygen-rich stream. Perhaps the most obvious is to use an adsorber which has a higher affinity for oxygen than for other atmospheric components, which will remove oxygen from air pumped through it on the adsorb cycle, and then desorbing

an oxygen-enriched gas stream for use and/or storage. This type of cycle has been described using "molecular sieve carbon" as adsorbent (11-13) or with natural coals (10). Unfortunately, the specificity of these adsorbers appears to be low, and consequently the purity of the product is not very high. Far more common are systems which selectively adsorb nitrogen from dry carbon dioxide-free air, producing a product stream consisting primarily of oxygen (up to 95% pure), with argon as the principal impurity. Several excellent reviews of the theory and practice of systems based on nitrogen adsorption are available (4,14,15) as well as numerous patents outlining different adsorb/desorb/regenerate cycles with varying claims of purity and production rates (6,11,13,16-18). The best units appear to be small scale (0-40 ton/day) with oxygen concentration in the product gas stream of 90-95%. Plants on the larger end of this scale are used for biological or ozone treatment of wastewater, bleaching and other chemical oxidation processes, or smelting (14). Smaller units can be envisioned in more mobile applications; for example, the U.S. Armed Forces have been evaluating molecular sieve oxygen generators for production of breathing oxygen in aircraft (19,20).

Pressure swing systems have the advantage of being very flexible in terms of scale, and also use relatively inexpensive adsorbents. The major technical requirements are pressurizing and/or evacuating capability and initial scrubbing to remove carbon dioxide and water. Of all the systems studied here, pressure swing systems are the closest to being reduced to practice, with some commercial plants in place and operating (4b). This type of system, especially one based on nitrogen adsorption, suffers from a severe drawback, however. The problem is that any impurities in the feed gas which are not strongly adsorbed will be present, and perhaps even concentrated, in the product stream. While this may not be a severe problem in wastewater treatment or chemical oxidation applications, the presence of toxic impurities in life support oxygen is definitely not

desirable. Consequently, pressure swing systems are best left to supply technical oxygen demands, while using other systems to furnish oxygen for life support purposes.

Type IB: Closely related to processes which rely on physical adsorption are those that utilize the ability of molecular oxygen to reversibly form adducts with certain chemical compounds. This process, which will be called chemical absorption, generally uses a transition metal coordination compound as the absorber. The study of oxygen binding to metal complexes has become of great interest over the past three decades (21), and some excellent reviews dealing with oxygen carriers and reversible binding exist (22-26). Much of this increased interest is due to the emergence of bioinorganic chemistry as a field of endeavor and the concomitant interest in model systems for the binding of oxygen in biological systems (24-26).

Consequently, there has been a sizeable amount of research involving hemoglobin, which serves as an oxygen transport system in vertebrates (27), and its active factor, protohemin (28). Most research in this area has been done in order to better understand oxygen binding to hemoglobin, but some attempts to design and build modified iron porphyrins to serve as reversible binding agents in aqueous solution (29-32) have been undertaken. In most cases the strategems adopted were successful at low temperatures, but led to decomposition at room temperatures. Some investigators have substituted other metals for iron, most notably cobalt (33-35) manganese (36,37) and ruthenium (38), usually to serve as model compounds for biologically important heme proteins.

Beside those complexes related to hemoglobin, the most extensively studied transition metal compounds are those based on cobalt(II). As with porphyrin systems some are related to biological complexes (39) or use biomolecules as ligands (40-43). Other studies have involved phthalocyanines (44,45), chelating

amines (46,47), macrocyclic tetramines (48,49), or other chelates (50-54). Most of these complexes have only been of academic or theoretical (55,56) interest, although some have seen limited use as catalysts in organic oxidations (45,57). Most of these studies of classical (Werner-type) complexes likely derive from observations of Frey in 1852 that certain cobalt ammine complexes reacted reversibly with oxygen (58) and more recent studies of oxygen binding by some cobalt - Schiff base complexes reported by Tsumaki in 1937 (59).

This last general class of compounds has seen the lion's share of applied research on all cobalt complexes, and has actually been used in a practical system. Most of the studies followed Tsumaki and relied on N,N-ethylenebis(salicylideneiminato)cobalt(II), Co(Salen), or substituted derivatives (60). Early basic research by Tsumaki (59) and Calvin (61) has been followed by extensive investigation of the effect of substitution on the degree and strength of cobalt-oxygen binding (62-68). Of greater interest to this study is the applied research which has paralleled the basic investigations.

There was intensive research during World War II to develop a method of supplying oxygen for the armed services to replace steel pressure cylinders. End uses envisioned encompassed medical and fabricating activities, and the aim was to develop a portable oxygen generator for field use; Co(Salen) was selected as a promising absorbent. A review of the research leading to the oxygen generator, including a bibliography of technical reports, was published shortly after the war (69).

The system functioned by using solid Co(Salen) to absorb oxygen from air at 80-100 psig and 50-90°F. Once saturated (oxygen content 4.0% by weight), the bed was subjected to temperatures of 200°F or above and pressures of 1 atmosphere or less to desorb the oxygen. The final pilot system had three beds which were cycled so that at least one bed was desorbing at all times. The unit was

installed on a destroyer tender and produced up to 350 cubic feet of 99.5% pure oxygen per hour for cutting and welding. Mechanical malfunctions terminated the experiment after four months, but "the unit appears to have been well received on the ship" (69). Apart from these technical problems, the system appears to suffer from one other major problem, in that repeated absorption/desorption cycles led to loss of capacity, presumably through oxidative decomposition of the absorbent.

Research continued into the next decade to attempt to optimize the system. An excellent review including an annotated bibliography is contained in a Bureau of Mines circular (70) reporting on the investigation of metal chelate sorption as a means for producing oxygen required for coal gasification; it was concluded that the process was not economically feasible. Since that time the emphasis of applications research appears to have shifted to more mobile situations.

Because of operational and logistics problems associated with liquid oxygen breathing gas supply systems, self-contained oxygen generators are desirable. A temperature cycled absorbent system similar to that outlined above, but using cobalt(3-fluoro-Salen) ("fluomine"), apparently has been one of the front runners in a joint Navy/Air Force development effort (71). The fluomine system suffers from the same problem as its parent system outlined above, in that adsorb/desorb capacity decreases with increased use, although the rate of decomposition is slower. Tests of purity indicate that the major contaminants in oxygen desorbed from fluomine beds are acetaldehyde (10 ppm), carbon monoxide (50 ppm), carbon dioxide (100 ppm), and water (1%), although none were judged to adversely affect the subjects breathing the oxygen (72,73). Of greater concern is the fact that organic contaminants in the supply air can be concentrated up to eight-fold in the product oxygen, raising serious questions as to the ultimate usefulness of this method for supplying breathing oxygen.

Other complexes have served as vehicles for reversible oxygen binding including low valent rhodium (74-76) and iridium (77,78) complexes in non-aqueous solvents, led by Vaska's report on $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (79). Non-heme iron (80-82) and ruthenium (83) complexes can also exhibit this type of behavior. A number of manganese complexes (84-87) also exhibit reversible oxygen binding in solution, but only one (88), a manganese-tertiary phosphine complex MnLX_2 (L=phosphine, X=anion), appears to have demonstrated solid state binding behavior. None of these examples has undergone the rigorous engineering study that $\text{Co}(\text{Salen})$ and its derivatives have, and so it remains to be seen whether any of them holds the key to solving the current problems in transition metal complex storage agents.

A novel way of sequestering monomeric transition metal complexes to improve their oxygen binding characteristics is to attach them to some sort of polymeric material. When this approach is taken with iron porphyrins, both capacity and rate of oxygen uptake is increased (89,90) and formation of the inactive μ -oxo dimer is not found (91), a reaction which usually plagues dissolved monomeric heme complexes. Cobalt-Salen complexes have also been attached to polymeric backbones and reversible oxygen binding was still observed (92,93). The drawback to these types of polymeric agents is the lowering of the oxygen capacity of the compounds on a per gram basis due to the addition of the polymer backbone. A system which is less troubled in this regard involves the complexation of metal ions by a family of polymeric oxime-type ligands, where the ratio of metal to polymer is higher than in the cases above. Most of the work has been done on copper complexes (94,95) but other metals, most notably iron, cobalt, nickel (96) or palladium (95) also reversibly bind oxygen in this form. The study of these systems has not yet focussed on engineering and development, so conjecture about eventual applications would be speculative at best, but it seems safe to say that they would be similar to those of other transition metal-based systems.

Type II: Next we consider those processes in which dioxygen is stored in a chemically bound form, but at the expense of its oxygen-oxygen bond. The most prominent of this type are those which utilize metal oxide equilibria to store oxygen. Illustrative of these is a process based on a reversible reaction of barium oxide (reaction 1) first observed by Boussingault in 1851 (97).



The rates of the reactions involved in this equilibrium are reasonable only at relatively elevated temperatures (700-800°C). Practical difficulties barred commercial utilization until approximately forty years later. At that time the Brin Oxygen Company was formed to utilize reaction 1 to separate oxygen from air. The Brin process operates at a constant temperature and relies on changes in pressure to determine the relative position of the barium oxide-barium peroxide equilibrium. At high pressures, oxygen is absorbed into the reaction mass from air in contact with it. Reducing the pressure (in the absence of air) results in the evolution of oxygen. This method was used commercially to separate oxygen from air for nearly twenty years until the more economical Linde liquification process replaced it.

Recently attempts have been made to improve the performance of this process by increasing the rates of reaction in each direction and reducing the operating temperature. To accomplish this, barium oxide was combined with other metal oxides (97). Of the numerous main group and transition metal oxides investigated, only La_2O_3 and MgO had any noticeable effect and for these the improvement was marginal at best. Other metal oxides have been tried, with some success. The activity of the strontium oxide-peroxide storage system is increased by admixtures a few mole percent of other metal ions, most notably sodium, copper and nickel (98). The best activities obtained are still only a factor of four better than

those obtained with the barium oxide-peroxide system, although the temperature required is reduced to 325°C. Short-term stability appears to be reasonable.

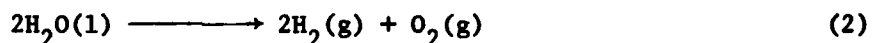
A thermal swing process using praseodymium oxide as the absorber has been proposed (99), but recent patents indicate that oxide solid solutions of praseodymium and cerium (100) are a great improvement, requiring much lower temperatures (400 vs. 900°C). The rates are again comparable to those found with the Brin process, and the stability of the system is excellent, with no reduction in performance over 7000 cycles (594 hours elapsed cycle time). Water and carbon dioxide inhibit the reactions but this effect can be substantially eliminated by doping the reaction mass with 0.4 weight percent silver. The processes above are fairly straightforward, involving only pressure and/or thermal swings of a metal oxide bed. Other more involved systems have been proposed. A process based on the mercury/mercuric oxide system has been patented (101) in which the first step is the reaction of hot mercury vapor (400-500°C) with air to form mercuric oxide, which can then be separated in a cyclone separator. The solid HgO is then heated to above 500°C in the absence of air to reform mercury vapor and pure oxygen. The products are quickly cooled to prevent back-reaction and the metallic mercury is vaporized and reused in the cycle. This type of process with its repeated heating and cooling, and consequent energy losses, is not likely to be a viable candidate in the near future (this apart from the question of traces of mercury vapor in the product oxygen).

The other, bed types, of metal oxide oxygen storage system have received more serious engineering study (102-104). Most of these process engineering patents specify a particular bed composition, usually based on barium oxide, and then concern themselves primarily with the details of the heating and cooling and/or pressure changes necessary to optimize adsorption and desorption. The same kinds of problems found in adsorption and absorption processes with bed

temperature control and pressure and vacuum requirements apply to these chemical processes as well, except that temperature control is more critical since the absorption step is generally exothermic and elevated temperatures could sinter the bed. Theoretical studies of metal oxide equilibria continue (105,106) but are not likely to uncover a system that offers more than a marginal improvement over existing processes.

Type III: The third general class of systems for storage of oxygen are those which rely on its generation from a cheap or easily reformed starting material. Most of the illustrations set forth below focus on the generation of oxygen from water, which is perhaps the cheapest common oxygen-containing chemical and thus has received the most attention. Other oxygen-containing compounds would also work if there were a cheap source available. The likely reasons for water's predominance in this class of processes are its density, ease of handling, and high oxygen content. If all of the oxygen in water can be recovered, the effective oxygen storage density is 0.89 g/cm^3 (55 lb/ft^3).

Methods for generating oxygen from water can be divided into two general categories. The first, electrolytic methods, encompasses those processes which separate water into its constituent elements through the use of an electric current. In these methods, the primary consideration is the cost and availability of electric power. The theoretical requirement for reaction 2 is 1.23 volts



with 386,000 coulombs required for every mole of oxygen produced, leading to an energy requirement of 475 kJ/mole O_2 . In reality this requirement is much higher, because actual operating voltages for electrolysis schemes are seldom less than 2.0 volts. NASA has funded some developmental research on water electrolysis (107-109). Two types of system have resulted from this research. One, developed

by General Electric (107) is based on a solid plastic sheet with a cation exchange function (by virtue of the incorporation of perfluorinated sulfonic acid groups) which is saturated with water. Power is fed to electrodes in contact with either side of the electrolyte sheet and hydrogen is evolved at the cathode and oxygen at the anode. The product oxygen is 99.7% pure with less than 2000 ppm nitrogen and 1000 ppm carbon dioxide. Lockheed has developed a system based on a concentrated (7 molar) potassium hydroxide electrolyte which is recirculated. The original concept led to a generation of hydrogen and oxygen (108) but later refinements allow the congeneration of dinitrogen gas at the anode by using a water/hydrazine mixture as the cell feed (109). In both cases, noble metals (e.g., platinum or iridium) are required as electrodes to reduce overvoltages to acceptable levels. Although noble metals are specified as electrode materials in the reports on these systems, some independent research is going on to produce still better electrodes, especially for oxygen evolution (110).

While these electrolysis systems work well, they suffer from some major drawbacks. The primary problem is power; electricity is a very expensive form of energy because of the inefficiencies involved in generating it. Processes such as these which are energy intensive will be practical only where the cost of power generation is less important, for example, in space. The second major problem is the large amounts of rare metals needed to construct a large operating system. This will probably restrict electrolysis to smaller volume applications, such as life support. Other problems in fabrication of cells and product gas separation exist, but are likely to be solved as engineering studies progress.

The second general type of water splitting systems are those that rely on thermal energy for its decomposition. The same energy requirement exists

as for electrolytic generation, but thermal energy sources are in general less expensive than electrical ones. Two primary approaches to thermal splitting have been developed. The first relies on direct splitting using high temperatures. At temperatures of 2500 °K gaseous water is in equilibrium with various fragments, including atomic and molecular hydrogen and oxygen, and hydroxyl radicals (111). Fractionation of this complex mixture to separate the oxygen and hydrogen can be accomplished by effusion of the lighter components (H and H₂) through a microporous membrane (111,112). Oxygen can then be separated from the uneffused material. The high temperatures required for this reaction are an obvious drawback, and are reasonably generated only by a concentrating solar collector (113,114).

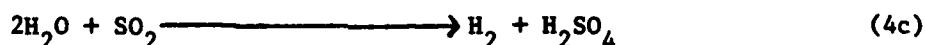
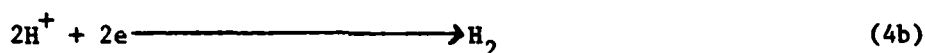
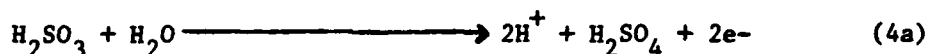
Recent calculations indicate that one can make use of oxygen's paramagnetism to reduce the temperature required to effect the splitting of water (115). Application of a magnetic field to water tends to cause its decomposition by shifting the equilibrium (reaction 2) in the direction of its paramagnetic product. Calculations indicate that this can be accomplished at 600 °K with a field of about 10,000 tesla (10^8 gauss). The process would have nearly Carnot efficiency, but unfortunately, the requisite magnetic fields are not at present attainable.

The other approach to thermal splitting of water is through the use of a thermochemical cycle. In principle, a series of reactions is set up such that the sum of the reactions is just the cleavage of water, reaction 2 above. Many different cycles are of course, possible. Patents have been issued for many types, ranging from iron chloride/oxide cycles (116,117) to those involving sulfur (118) or carbon (119) oxides. The iron-chlorine family of water splitting processes is representative of the many transition metal cycles which have been proposed. This family can be separated into five typical groups: Chlorination,

thermal decomposition, hydrolysis, regeneration of chlorinating reagent, reduction. A recent feasibility study concluded that reaction rates are high enough and yields are adequate (120). It was also concluded that the large number of possible variations in the iron chlorine family will allow for process optimization. A typical cycle is outlined in Scheme I. Many others are possible. The cycles need not be so complex, however. Westinghouse has developed a two step cycle based on sulfur oxides (121). In the first step, sulfuric acid is decomposed at temperatures above 1000 °K (reaction 3). The sulfur dioxide so produced is then used to depolarize the anode of an electro-



chemical cell (reaction 4a) with the accompanying cathode reaction being reduction of protons to hydrogen (reaction 4b), resulting in the net reaction (4c) for the cell. The potential under standard conditions is theoretically

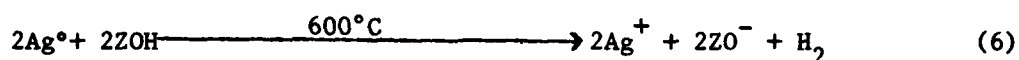
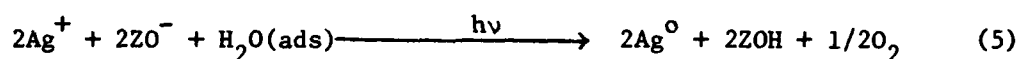


-0.17 volts, but under operating conditions using 70-80 weight percent acid electrolyte, the actual operating voltage is -0.80 volts.

Common problems plague all of these thermochemical cycles. One is the necessity for high temperatures in at least one step of the cycle, high temperature heat being relatively more expensive than that generated at lower temperatures. A second difficulty lies in the need for quantitative yield for every reaction in the cycle. With anything less than 100% yield, material balance becomes critical quite quickly. The third problem is one separations; often

intermediates must be separated to be of further use in the cycle. Any separation process adds energy requirements and possible material losses to the system.

An interesting alternative to the typical thermochemical cycle has recently been advanced (122). It involves the hydration of a sample of silver-substituted Type Y zeolite ($\text{Ag}^+\text{-Y}$) and its subsequent exposure to sunlight (reaction 5), which yields oxygen gas, reduced silver, and protonated zeolite. The original



(ZO^- = zeolite oxygen atoms)

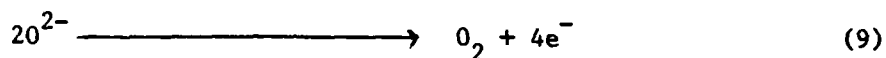
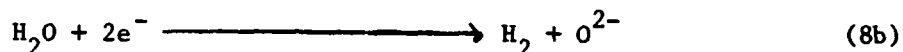
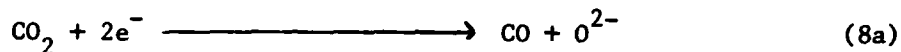
zeolite can be regenerated (accompanied by hydrogen evolution) by heating to 600 °C (reaction 6). A gradual loss of activity is observed, however, due primarily to dehydration of the zeolite (reaction 7) or to silver metal



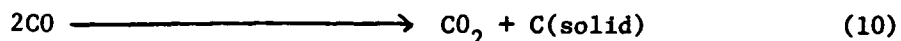
sintering out of the zeolite during either step of the cycle. If these problems can be solved, the zeolite cycle will be less prone to the material loss problems that interfere with the other types of cycles.

In addition to these systems which rely on the decomposition of water alone, there are some being developed to use a combination of carbon dioxide and water. These processes use an electrochemical method to generate oxygen at the anode and reduced carbon and hydrogen species at the cathode. Developed under contracts from NASA, these systems are intended to recover and recycle oxygen in totally self-contained environments, such as spacecraft. The most feasible of the two has seen scale-up to a full-sized, six-man unit (123). Carbon dioxide and water vapor are fed to the cathode of an electrochemical cell where they are

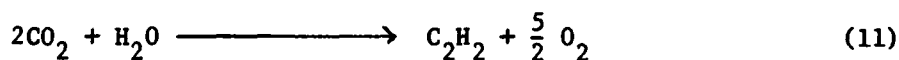
reduced (reactions 8a,b). The cell is based on solid zirconium-yttrium oxide electrolyte which transports oxide (O^{2-}) ions at the operating temperatures of 875 °C. At the anode reaction 9 occurs, producing oxygen gas. The carbon monoxide is separated from the hydrogen (which is vented) by a palladium



membrane and disproportionated in a high temperature carbon deposition reactor (reaction 10) with the carbon dioxide so produced being recycled for another



pass through the system. The electrolyzer voltage is 1.75 volts/cell and 1,296 cells of 6 cm² area each are enough to produce the 12.5 lb/day oxygen required by the six man rating. The other method (124) is based on the electrolysis of water and carbon dioxide according to reaction 11 in a cell



based on a molten lithium-potassium oxide-carbonate-chloride electrolyte. This cell appears to have more problems than the first, primarily because of the corrosive nature of the electrolyte at the operating temperature of 430 °C. Both systems have sizeable thermal and electrical energy requirements and are not thus likely to be competitive except in applications where recovery of as much oxygen as possible is desirable.

Type IV: The final general class consists of those systems which are in reality continuous separation methods, but can be coupled with ordinary pumped

storage to construct a system which generates pure oxygen. Many continuous separation techniques use membranes of one sort or another. The most obvious technique is that of selective permeation, where a membrane is chosen which is more permeable to one gas in a mixture than the others. The theoretical and technical details of membrane separations are reasonably well understood (125) and it appears that silicone rubber and substituted poly(phenylene ether) (125,126) are the materials of choice for oxygen separation, with the latter type being somewhat preferred. Patents are also appearing describing complete systems for oxygen separation (127). One potential drawback to the use of selective permeation is that for simple systems of one or two stages oxygen concentrations in the product stream are only about 50 percent (126,127). While this is adequate for some medical uses envisioned (127) it falls short of the enrichment provided by most of the systems discussed above.

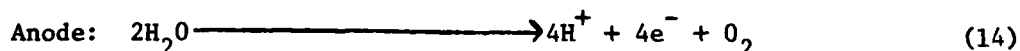
An improvement on the permeation technique can be accomplished by using a film which allows oxygen to pass, but substantially excludes all other gases normally present in air. Membranes can be constructed of various alloys of silver with other d-electron rich transition metals (128). At operating temperatures of 400-600 °C oxygen diffuses through 10 micron alloy films, while pure silver films apparently need to be 100 times thinner to function well. The method has promise, but little has been reported as to rates or purity of product.

While these selective permeation methods use passive transport (which may be chemical in nature for the silver films) a method which uses active transport has been developed which has proven to be more successful. One embodiment of this concept (129) relies on the reduction of oxygen to hydroxide ions (reaction 12) on the "air" side of the membrane, transport of the hydroxide ions



so produced across the membrane, and their re-oxidation on the other side of the membrane (reverse of reaction 12) to produce essentially pure oxygen. The membrane in the case is an aqueous alkaline hydroxide/asbestos matrix sandwiched between porous silver and catalyzed porous nickel electrodes. The only requirements are electric power to drive the transport and some means to control the humidity in input and output streams.

Similar in concept is a process based on a cation exchange solid polymer electrode (130a-d) in which the membrane is a Type "R" perfluorinated sulfonic acid ion-exchange membrane. Just as in the alkali-based cell described above, electrical power is used to electrochemically "pump" oxygen from an air stream through the electrolyte, but the electrode processes (reaction 13,14) are different since the membrane is designed for cation transport.



The concentrator cell is shown schematically in Figure 2. This type of oxygen concentrator has been developed by General Electric to serve as the separation unit in a self-contained aircraft oxygen system (71,130) which will supply up to 4.6 lb/hr of 99.5 percent pure oxygen for the crew of an F-4C or other fighter-type aircraft. Unlike the pressure swing adsorption or fluomine-based systems described earlier, the electrochemical concentrator needs no additional compressor since it can generate oxygen at pressures up to 380 psi. At this pressure, the accumulator is sized so that there is enough reserve oxygen capacity for emergencies. The system operates on a closed loop rebreather

cycle using a scrubber to remove carbon dioxide and make-up oxygen supplied by the concentrator.

Other continuous generation methods are not as well developed. Oxygen gas is quite soluble in fluorocarbon or silicone liquids, and methods of oxygen transfer based on that property have been proposed. The most obvious is to just use the liquid as a transfer medium. Fluorocarbons have found some utility as perfusion agents or in blood replacement and oxygenation (131). However, a potentially more useful application of this solubility to effect a separation is outlined in a recent patent (132). In the proposed process, air is dissolved in a fluorocarbon or silicone liquid under pressure (to increase the solubility). The pressurized stream is then passed between the poles of a strong magnet where oxygen will collect in the magnetic field due to its paramagnetism. The bubbles of pure oxygen are to be collected in some unspecified manner, and the working fluid is recycled, resaturated with air, and sent through the process again. This process is obviously quite far from actual use and will probably suffer from many of the same problems as other magnetic separation processes, in which it has been necessary to fill the space between the pole pieces with steel wool in order to generate high enough field gradients to effect the separation, since the important parameter is not field strength, but the gradient. However, this process does serve to illustrate the innovative approaches that are being considered to effect a separation of oxygen from air.

CONCLUSIONS

There exist many alternatives to cryogenic liquification methods for the generation and storage of molecular oxygen. While none of these pose a serious threat to cryogenic methods as a means for large-scale production; there are many small-scale applications where one or more of them may prove to be competitive.

Pressure swing adsorption units are likely candidates to meet small scale (up to 40 ton/day) technical oxygen requirements. The best systems are based on the adsorption of nitrogen from air to leave a product stream which is 90-95% oxygen. If a continuous supply is required, from two to four adsorber beds will be needed to run on a staggered adsorb/desorb cycle. We can expect to see more of these plants supplying process oxygen on a small scale, mostly as dedicated units.

Chemical absorbent based systems have the potential to supply higher purity oxygen than nitrogen adsorption units. However, problems with absorber decomposition keeps these systems from being viable at present. Although the prototype complex $\text{Co}(\text{Salen})$ and its derivatives are not likely to form the basis for a competitive system, it may be possible to identify a complex where decomposition is not an inevitable consequence of oxygen binding. If it is desired to use this type of system, long-term stability studies (including repeated cycling) on a number of candidate compounds will be necessary; manganese phosphine dihalides (88) are the most attractive possibility at this point. Serious consideration should be limited to those complexes that bind oxygen in the solid state, since engineering and economic considerations rule out solution-dissolved species for most applications. If a satisfactory absorber is found, uses for a thermal swing chemical absorber system are likely to be even smaller

scale than those found for zeolite-based adsorption systems and will likely be to supply needs for purer oxygen than is available from adsorption systems.

Life support oxygen is probably best supplied by one of the electrolytic methods. If air is available, the best method is likely to be the electrolytic membrane concentrator based on a solid polymer electrolyte (130). This system is particularly attractive because it does not need additional mechanical compression capability to generate useable pressures. For situations where an oxygen-containing atmosphere is not available, one of the systems based on the co-electrolysis of carbon dioxide and water seems attractive. Of the two reviewed here, the one based on the Zr-Y oxide electrolyte (123) is most promising. It appears to be able to accomodate varying carbon dioxide/water ratios and seems to have fewer technical problems associated with it. Although it allows total recycling of oxygen consumed in aerobic metabolism, the generation of oxygen from two such stable chemicals as CO_2 and H_2O will extract a sizeable energy penalty. This will likely mean that this method will effectively be limited to outer space life support systems.

Of the other systems examined in this study, none seems to have the potential for future development and use that the four mentioned above do. Further research may alter that conclusion, or a new concept in oxygen generation and/or storage may be unearthed, but based on the data available, these seem the best choices. Pressure swing adsorption using molecular sieves is already a commercially viable process; only time will tell whether the other three are also successfully developed.

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SCHEME I^a

	Optimum temperature °K	^b ΔH_{rxn} kJ/mole
$3\text{FeCl}_2 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$	1200	+195
$\text{Fe}_3\text{O}_4 + 8\text{HCl} \longrightarrow 2\text{FeCl}_3 + \text{FeCl}_2 + 4\text{H}_2\text{O}$	650	-112
$2\text{FeCl}_3 \longrightarrow 2\text{FeCl}_2 + \text{Cl}_2$	600	-25
$\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + 1/2 \text{O}_2$	1200	60
<hr/>		
Net $\text{H}_2\text{O} \longrightarrow \text{H}_2 + 1/2 \text{O}_2$		

^a Data from Ref. 120.

^b At the listed optimum temperature.

FIGURE CAPTIONS

Figure 1. Typical adsorption isotherms. x = adsorb conditions, ● = desorb conditions. (Adapted from Ref. 4b).

Figure 2. Schematic diagram of an electrochemical concentrator cell showing electrode reactions and transport.

